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EFFECTS OF CO-CATALYSTS ON THE DIMERIZATION OF ISOPRENE BY BIS(TRIPHENYLPHOSPHINE) NICKEL DICHLORIDE-AMINE-SODIUM BOROHYDRIDE SYSTEM

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A proper amount of water was found to enhance significantly the catalytic activity of $Ni(PPh_3)_2Cl_2$-Amine-$NaBH_4$ for the dimerization of isoprene. The principal products were linear dienes with n-propylamine, and cyclic ones with pyridine and its derivatives, respectively, but almost independent on the amount of water.

Dimerization reactions of conjugated dienes have been intensively studied using various catalyst systems that contain transition metal ions of various coordination structures$^{1)}$. The complexes containing zero-valent nickel have been reported to yield cyclic dimers from dienes in aprotic solvents, and linear ones in protonic solvents$^{2)}$, although $Ni(PPh_3)_2X_2$(X:halide) reduced by Grignard reagent gave a linear dimer from isoprene in tetrahydrofuran$^{3)}$. We previously reported that some amines enhanced significantly the catalytic activity of $Ni(PPh_3)_2Cl_2$ reduced by $NaBH_4$ for the dimerization of isoprene$^{4)}$. However, the system showed only a very small activity on some occasions. Such an activity decrease may have a relation with the amount of water present in the system. The authors report its significant effect on the activity in the present paper.

$Ni(PPh_3)_2Cl_2$ was prepared according to the method described in the literature$^{5)}$. Isoprene was dried with anhydrous calcium chloride and molecular sieve, and then distilled under nitrogen. Amines were dried with barium oxide and distilled under nitrogen. The dimerization reaction was carried out in a sealed glass tube that was kept in an oil bath at a constant temperature of 80° for 24 hr. In a typical experiment, after being filled with nitrogen, the glass tube was charged with 0.5 mmol $Ni(PPh_3)_2Cl_2$, 1.5 mmol $NaBH_4$, 1 ml isoprene, 1 ml amine, 5 ml benzene as a solvent and 1 ml n-pentane as a internal standard, and then a certain amount of water was injected with a micro-syringe. After the content was frozen in liquid nitrogen, it was degassed in vacuo to be sealed. After the reaction mixture was washed with 1N-HCl to eliminate the amine from the products, a mixture of isoprene oligomers was analyzed by a gas-chromatograph using a column packed with Apiezon Grease L.

Identified products from the present study were 2,6-dimethyl-1,3,6-octatriene (DMOT), dimethyloctadienes(DMOD) such as 2,6-dimethyl-2,6-octadiene, 2,7-dimethyl-1,6-octadiene and 2,6-dimethyl-1,6-octadiene, dimethylcyclooctadienes(DMCOD) such as 2,5-dimethylcyclooctadiene and 2,6-dimethylcyclooctadiene, and dipentene(DP). Addition of amine to isoprene was not observed under the present conditions$^{6)}$.

The dimerization was quite slow at 80° when the reactant and the solvent were used immediately after the drying treatment. Further drying brought about a less

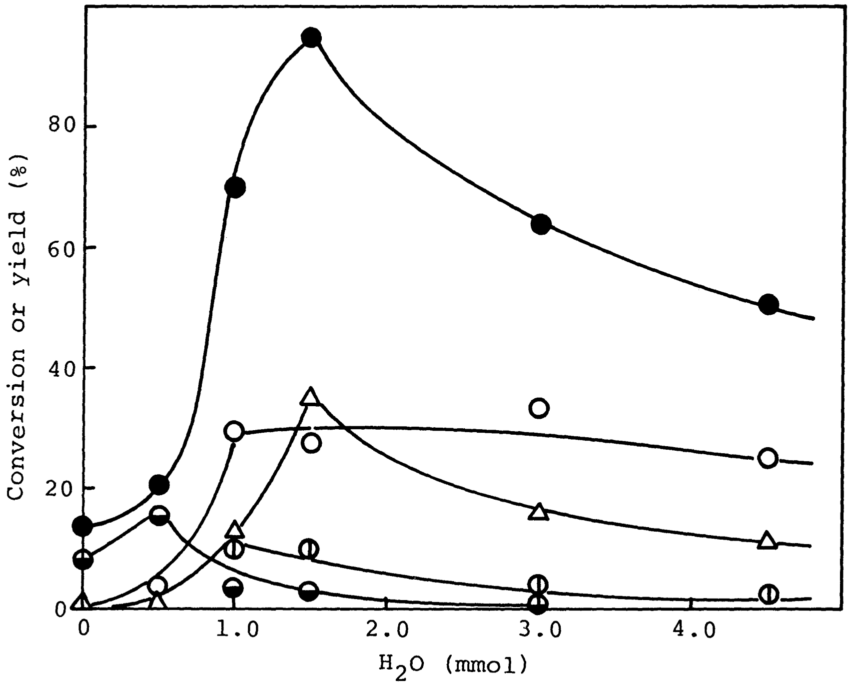

Fig. 1. Effect of water on the catalytic activity for the dimerization.
n-Propylamine ; 1 ml, $Ni(PPh_3)_2Cl_2$; 0.5 mmol,
$NaBH_4$; 1.5 mmol, Isoprene ; 1 ml,
n-Pentane ; 1 ml, Benzene ; 5 ml,
Reaction temp. and time ; 80°C, 24 hr
● ; conversion, ○ ; DMOD, △ ; DMOT,
◒ ; DP, ⦶ ; DMCOD

activity. In contrast, a catalytic amount of water was found to accelerate the reaction significantly. The effects of water amount on the catalytic activity are shown in Fig. 1, where n-propylamine was used as a promoting amine. The conversion of isoprene increased with the more amount of water and reached the maximum of 94.6% at around 1.5 mmol which is equivalent to the amount of $NaBH_4$. Among the products, the linear dimers such as DMOD and DMOT were main products when more than 1.0 mmol water was added, whereas DP was the main one at a small amount of water although the yield was quite low. The yield of DMOT depended markedly on the concentration of water, however that of DMOD was rather independent of the amount of water except for its quite low concentration.

Promoting effects of water are further shown in Fig. 2 where 3-picoline was used as an amine. In common to other cyclic amines, the enhancement of activity was quite similar to the case of n-propylamine, however the cyclic dimers such as DMCOD increased significantly in these cases. Although the yield of DMOT was little, it increased monotonically with the amount of water added in this case, too. The conversion without water was ca. 1.5% in this case. This value was significantly smaller than that of the case of n-propylamine. A proton donor may be more essential

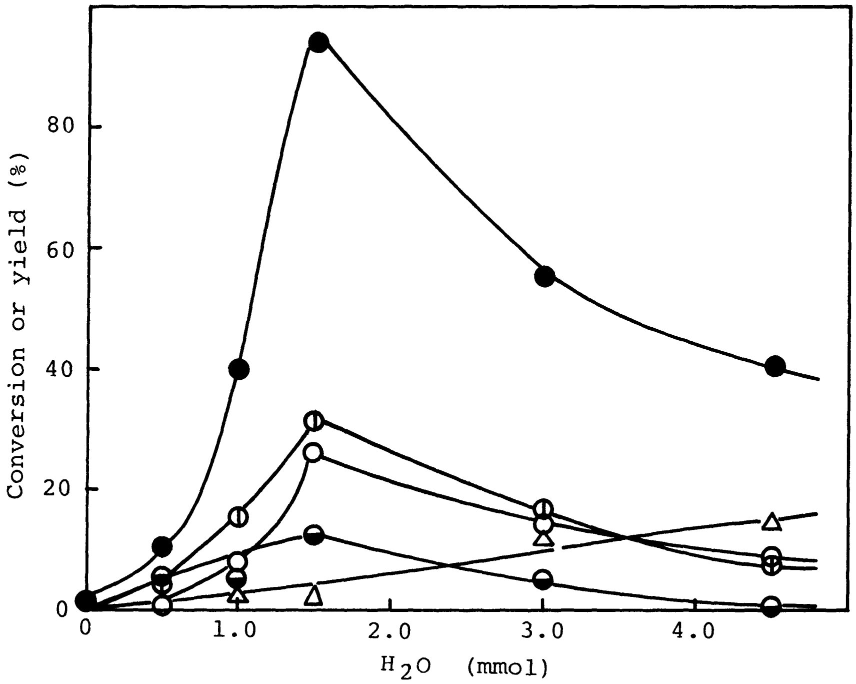

Fig. 2. Effect of water on the catalytic activity for the dimerization.

3-Picoline ; 1 ml, $Ni(PPh_3)_2Cl_2$; 0.5 mmol,
$NaBH_4$; 1.5 mmol, Isoprene ; 1 ml,
n-Pentane ; 1 ml, Benzene ; 5 ml,
Reaction temp. and time ; 80°C, 24 hr
●; conversion, ○; DMOD, △; DMOT,
⊖; DP, ⦶; DMCOD

Table. Effects of Co-catalysts

Co-catalysts	Yield(%)					Conversion
	DMOD	DMOT	DP	DMCOD	others	(%)
none	0.3	0.4	0.6	0.1	0.1	1.5
H_2O	25.9	2.2	12.2	31.5	21.9	93.7
CH_3OH	0.4	1.2	6.5	0.2	2.5	11.0
C_2H_5OH	0.9	3.3	14.4	4.3	1.5	24.5
$n\text{-}C_3H_7NH_2$	0.1	0.4	1.3	0.1	0.1	2.0
CH_3COOH	7.7	0.1	5.4	0.6	11.2	25.0

$Ni(PPh_3)_2Cl_2$: 0.5 mmol, $NaBH_4$: 1.5 mmol
Co-catalysts : 1.5 mmol, Isoprene : 1 ml, n-Pentane: 1 ml
Benzene : 5 ml, 3-Picoline : 1 ml
Reaction temp. : 80°C, Reaction time : 24 hr

in the case of the cyclic amine.

The effects of methanol, ethanol, n-propylamine and acetic acid instead of water were investigated in order to elucidate the role of water. The results are summarized in Table. They also showed accelerating effects except for n-propylamine, although they were less efficient than water. The product distributions were quite different from the case of water. For example, DP is the main product for alcohols, whereas DMOD is main for acetic acid. A considerable amount of unidentified dimeric products observed in the case of acetic acid are assumed the adducts of acetic acid as Hiembach et al. reported7). Such a co-catalytic effect of water has been observed in the co-dimerization of butadiene and ethylene catalyzed by σ-arylnickel (II)-$BF_3$8). However, its features seem somewhat different from those of the present case. The roles of the proton donors are now under investigation.

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